CONSTRUCTION OF MODEL STRUCTURES OF UPPER FREEPORT COAL EXTRACTS USING SOLID-STATE ^{13}C NMR CHEMICAL SHIFT CALCULATION

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INTRODUCTION

Many analytical techniques have been used for coal research and the analytical data have enabled the construction of model chemical structures of coal. The construction of model structure of coal is important in improving our understanding of the relationships between coal structure and its properties; this knowledge can lead to more effective and economical methods of coal conversion. Iino et al. investigated the extract fractions obtained from the extraction of Upper Freeport coal with a carbon disulfide/N-methyl-2-pyrrolidinone mixed solvent at room temperature and the fractionation with acetone and pyridine by using ^{1}H NMR, elementary analysis, SEC and hydroxyl group estimation.[1] Based on the structural parameters obtained, i.e., f_a(aromaticity), σ (the degree of substitution on aromatic rings) and H_{aru}/C_{ar}(the degree of condensation of the aromatic rings), Takanohashi et al. constructed the model structures of the extract fractions, as shown in Fig. 1.[2] Recently, for calculating the NMR chemical shifts of known molecular structures, several programs have been developed. We modified the chemical structure of Upper Freeport coal extracts constructed by Takanohashi et al. using the ^{13}C NMR chemical shift calculations. The purpose of the present work is to improve the model structures by comparison of actual and calculated solid-state ^{13}C NMR spectra.

EXPERIMENTAL

Sample: The extract (60 wt% on raw coal basis) from a carbon disulfide/N-methyl-2-pyrrolidinone mixed solvent extraction at room temperature for Upper Freeport coal was fractionated with acetone and pyridine into three fractions, i.e., acetone-soluble (AS), acetone-insoluble/pyridine-soluble (PS), and pyridine-insoluble (PI) fractions. These extract fractions of Upper Freeport coal were used as samples. Data on structural analysis of the extracts are summarized in Table 1.

NMR measurements: Solid-state ^{13}C NMR measurements were made by the SPE/MAS method using a Chemmagnetics CMX-300 NMR spectrometer. About 100 mg of sample were packed in the sample rotor. The measuring conditions were as follows: the 90° ^{1}H pulse width was 4 μ s; ^{13}C frequency, 75.46 MHz; spinning rate of MAS, 10 kHz; number of scans, 2000; and pulse repetition time, 60 s. Chemical shifts were calibrated with respect to tetramethylsilane using the hexamethylbenzene's methyl group peak at 17.4 ppm as the external standard.

Chemical shift simulations: Chemical shift calculations were carried out using ACD Laboratory CNMR predictor software. Thomas et al. calculated ^{13}C chemical shifts for some substituted pyridines using several NMR prediction programs and showed that the CNMR predictor gave the best results in their work.[3] Kohnert et al. evaluated and tested for prediction of NMR spectra of photosynthetic metabolites using the CNMR predictor.[4] The software allows treatment of molecules containing up to 256 carbon atoms. The software calculates chemical shifts by searching for similar sub-structural fragment with the corresponding experimental shift value in the internal database and evaluating the chemical shift value taking into account intramolecular interactions. Using the software, we calculated the chemical shifts of all carbons of each model structure constructed by Takanohashi et al.[2] Next, the calculated ^{13}C NMR spectra were obtained by considering an adequate line width to each peak and summing, supposing that all peaks were Gaussian peaks.(This process was performed by Spinsight ver.3.5.2 software.) The line width fitted to the actual spectra was adopted. For AS, PS and PI, the line width for aromatic carbon was 814 Hz, 1203 Hz and 1344Hz, respectively, and the line width for aliphatic carbon was 354 Hz, 460 Hz and 601Hz, respectively. As the fraction became lighter, the line width of each peak became narrower, with narrower lines for aliphatic than for aromatic carbon. Although, all aromatic or

aliphatic carbons may not have the same line width, it is time consuming to derive a line width for each carbon, so each one line width was used for aromatic or aliphatic carbon of the each extract fractions. By comparison with actual spectra, the model structures were modified. The chemical shifts were calculated again for the revised structures. By repeating this process, the best fitting structures were determined.

RESULTS AND DISCUSSION

Fig 2 shows the experimental NMR spectra of the extract fractions and the calculated NMR spectra for model structures of each fraction. For AS, with regard to the actual spectra, the model structure had high fractions for non-protonated aromatic carbon (125～140 ppm) and CH_2 carbon(15～25 ppm), and low fractions for protonated aromatic carbon(100～120 ppm), CH_2 carbon(30～45 ppm) and methyl carbon(0～15 ppm). We added methyl carbon to the model structure of AS and reduced the substituted aromatic carbon and β CH_2 carbon. The resulting structure of AS is shown in Fig. 3(a) and the calculated NMR spectrum for the revised model structure is shown in Fig.4(a) with the measured spectrum. For PS and PI, the model structures had high fractions for non-protonated aromatic carbon (125～140 ppm) and CH_2 carbon(35～50 ppm), and low fractions for methyl carbon(0～20 ppm). We added methyl carbon to the model structures of PS and PI and reduced the substituted aromatic carbon. Figs. 3(b) and (c) show the resulting structures of PS and PI that best fitted the actual spectra. Fig. 4(b) and 4(c) show the calculated NMR spectra of the revised model structures with the measured spectra. We modified all structures of extract fractions mainly by adding methyl and ethyl groups and reducing naphthenic ring structures. This indicates that the all initial structures lacked methyl and ethyl groups and were rich in naphthenic ring structures, which we could not distinguish by the previous analytical data. By these techniques, the correction of the model structures for the extract fractions could be made.

The chemical shift at 60 ～ 80 ppm corresponds to the aliphatic carbon connected with oxygen such as $-CH_2-O-$, which is thought to be important for the crosslink of coal. For the calculated spectra for PS and PI, the peaks appeared in this chemical shift range. Considering the crosslinks in coal, such oxygen containing methylene bonds possibly exist in coal, but the actual spectra showed no peak in this chemical shift range between aromatic and aliphatic carbon peak, and we cannot confirm the peaks. The amounts of the aliphatic carbon connected with oxygen may or can not be so large compared with the other forms of carbon, and the peaks may be overlapped, so in the actual spectra the peaks might not appeared.

Table 2 shows structural parameters of the revised model chemical structures. The values of f_a and H_{au}/C_a were almost similar between the initial and the revised model structures, but the values of σ and H/C were different. The values of σ were higher for the initial structures and the values of H/C were higher for the revised structures. This was because, in the modification process, we added some methyl and ethyl groups and reduced some naphthenic ring structures in order to fit the actual spectra. In this regard, further examination is required to coincide these data. However, relatively good agreement was obtained between the actual spectra and calculated ones by the new models.

CONCLUSION

The solid-state ^{13}C NMR spectra of the model structures for the three extract fractions were estimated using the NMR chemical shift calculation method. By comparison of the estimated spectra with the observed ones, some corrections were made to the chemical structure of models to fit their spectra, and we proposed the modified model structures based on NMR chemical shift calculations. The energy-minimum conformation will be calculated by the molecular mechanics and molecular dynamics

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Table 1. Structural parameters of extracts of Upper Freeport coal[2]

Sample	Ultimate analysis (wt%)[a]					Structural parameters					
	C	H	N	S	O[b]	M_n	f_a	H_{au}/C_{ar}	σ	H/C	molecular formula
Original coal	86.2	5.1	1.9	2.2	4.6					0.71	
AS	88.5	6.7	1.1	0.5	3.2	520	0.71	0.69	0.39	0.91	$C_{38}H_{34}NO$
PS	86.6	5.8	2.0	1.8	4.5	1270	0.78	0.72	0.51	0.75	$C_{92}H_{68}N_2O_5$
PI	85.8	5.0	2.1	1.1	6.0	2210	0.79	0.71	0.48	0.70	$C_{158}H_{110}N_3SO_8$

a)dry ash free

b)calculated as the difference

Table 2. Structural parameters of the revised model chemical structures

Sample	Structural parameters				
	f_a	H_{au}/C_{ar}	σ	H/C	molecular formula
AS	0.71	0.71	0.30	1.03	$C_{38}H_{39}NO$
PS	0.79	0.69	0.44	0.81	$C_{91}H_{74}N_2O_5$
PI	0.80	0.67	0.40	0.77	$C_{157}H_{121}N_3SO_8$

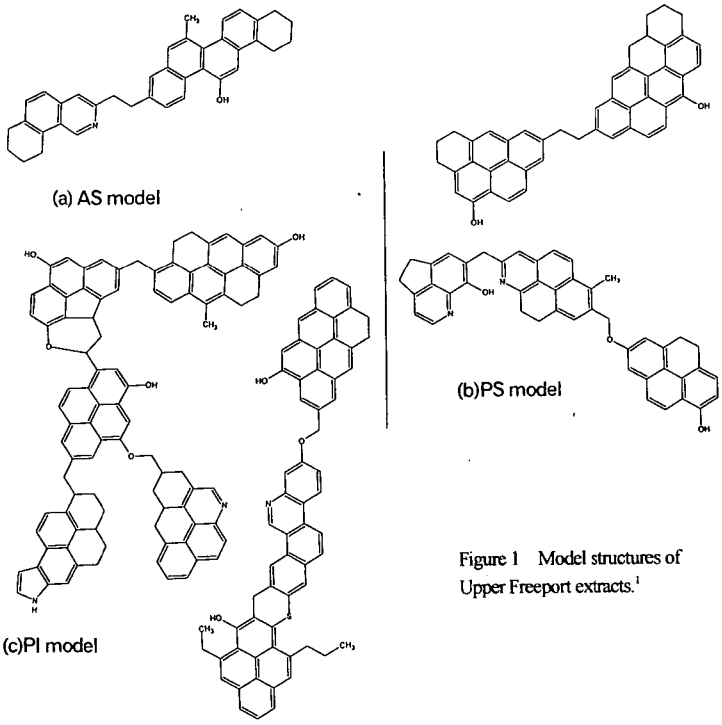

Figure 1 Model structures of Upper Freeport extracts.[1]

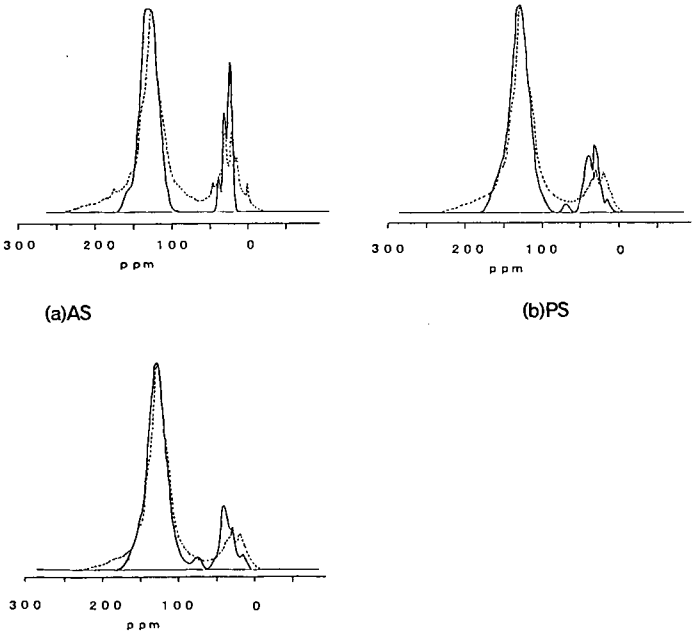

Figure 2 Measured SPE/MAS ^{13}C NMR spectra of solvent extracts(- - - - -) and calculated NMR spectra of model chemical structures(——).

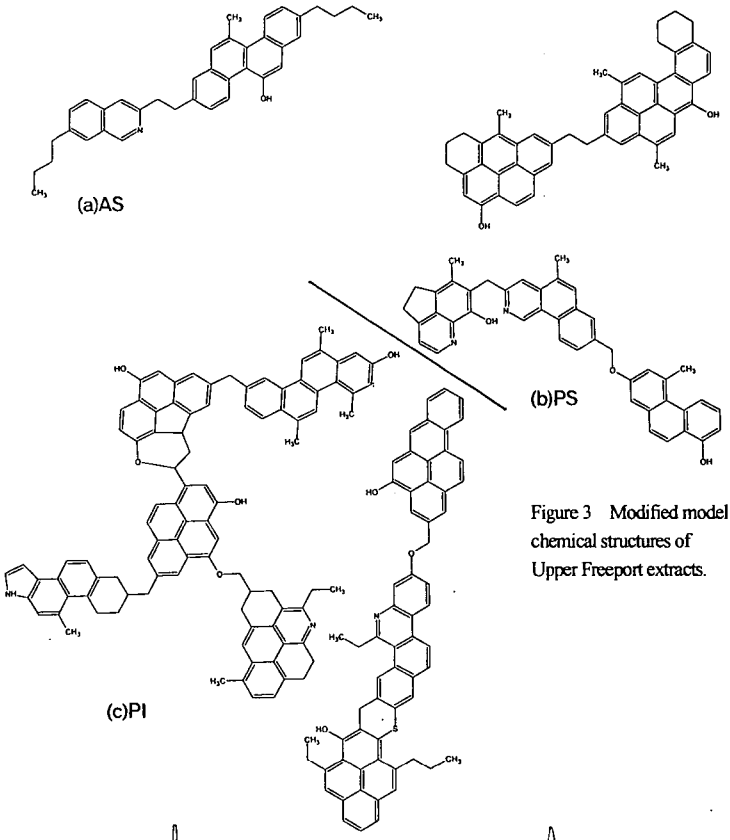

Figure 3 Modified model chemical structures of Upper Freeport extracts.

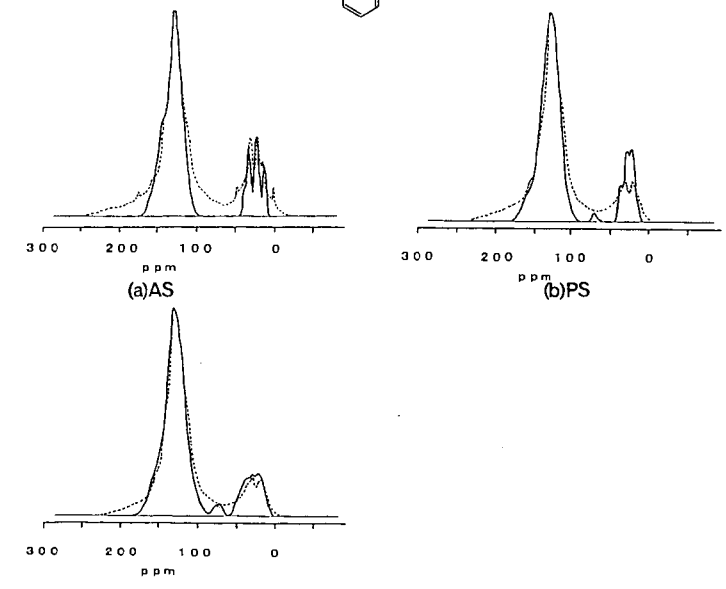

Figure 4 Measured SPE/MAS ^{13}C NMR spectra of solvent extracts(- - - - - -) and calculated NMR spectra of modified model chemical structures(——).